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PATENT SPECIFICATION

(11) **1 467 970**

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(21) Application No. 24839/74 (22) Filed 5 June 1974
(23) Complete Specification filed 2 May 1975
(44) Complete Specification published 23 March 1977
(51) INT CL² C08G 65/30
(52) Index at acceptance C3R 27K8F
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Process not used to remove catalyst

(54) PURIFICATION OF POLYETHERS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LTD., Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polymeric materials and more particularly to a process for the purification of polyethers.

It is already known to manufacture polyethers by the addition of one or more alkylene oxides to an active hydrogen-containing compound in the presence of a basic catalyst. Such polyethers are often required in extremely pure form and various purification procedures have been proposed, the main object of which has been to remove the basic catalyst residues. Known purification techniques include treatment with acids and with various absorbent materials. Such techniques have been effective in most cases but it has been observed that special problems can occur in the manufacture of polyethers of the block polymer type which contain blocks of oxyethylene units and blocks of other oxyalkylene units. Such polyethers are manufactured by adding ethylene oxide and another alkylene oxide in separate stages to an active hydrogen-containing compound, and, unless the oxyethylene content is high, they are usually clear liquids at normal temperatures. In some cases, however, it has been found that products are obtained which have a cloudy appearance and this is believed to be due to the presence of crystalline ethylene oxide polymers such as polyethylene glycol. In addition to being cloudy, these defective batches of polyether can be unsatisfactory in respect of their viscosity characteristics and chemical properties.

It has now been found that polyethers having the aforesaid defects can be rendered satisfactory by the purification procedure hereinafter described.

Thus, according to the present invention, there is provided a process for the purification of polyethers which are the liquid reaction products obtained by the sequential addition of ethylene oxide and at least one other alkylene oxide to an active hydrogen-containing compound, said process comprising treating the polyether with a mixture containing 1 part by weight of active carbon and from 2.5 to 7.5 parts by weight of synthetic magnesium silicate

The polyethers which may be purified by the process of the present invention have been fully described in the prior art. Broadly speaking, they are the products obtained by polymerising ethylene oxide and at least one other alkylene oxide in two or more separate stages in the presence of a compound containing one or more active hydrogen atoms in the molecule. Such polyethers are commonly used as surface active agents, lubricants and polyurethane intermediates.

Examples of other alkylene oxides which may be used in conjunction with ethylene oxide include propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide and epichlorohydrin.

The process of the invention is particularly suitable for the purification of polyethers which contain at least two hydroxyl groups per molecule and which are made by the addition of ethylene oxide and propylene oxide to a compound containing at least two active hydrogen atoms in the molecule. Examples of active hydrogen compounds which may be used in the preparation of such polyethers include water, ammonia, hydrazine, cyanuric acid, phosphorous, phosphoric or phosphonic acids, polyhydroxy compounds, for example ethylene glycol, propylene glycol, diethylene glycol, glycerol, trimethylolpropane, triethanolamine, pentaetrythritol, sorbitol, sucrose, phenolformaldehyde reaction products, resorcinol, and phloroglucinol, aminoalcohols, for example monoethanolamine and diethanolamine, polyamines, for example ethylene diamine, hexamethylene diamine, tolylene diamines and diaminodiphenylmethanes and polycarboxylic acids, for example adipic acid, terephthalic acid and trimesic acid. The ethylene and propylene oxides may be added to the active hydrogen-containing compound in any order

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and in two or more separate stages. Thus, propylene oxide may be reacted first followed by ethylene oxide or the reverse procedure may be used, optionally with further additions of the same or other alkylene oxides. In a further variation the active hydrogen compound can first be reacted with a mixture of ethylene and propylene oxides to form a random copolymer and then with ethylene oxide alone to introduce polyoxyethylene blocks into the polyether. The polyethers may have molecular weights of from 1000 to 10,000 and oxyethylene contents of from 5 to 50% by weight based on the total oxyalkylene content.

Before being treated in accordance with the present invention, the polyethers may have been subjected to standard purification procedures for the purpose of removing unreacted alkylene oxides and catalyst residues.

The synthetic magnesium silicate and active carbon used in the process of the invention are well known commercially available materials. The most suitable amount of the mixture of synthetic magnesium silicate and carbon to use in the process of the invention depends upon the degree of purification required and may be found by trial. In general, suitable amounts of mixture to use are in the range of from 0.5 to 15% by weight based on the weight of polyether being treated. It is preferred to use a mixture containing from 4.5 to 6.5 parts by weight of synthetic magnesium silicate for each part by weight of active carbon.

The purification procedure may be performed at normal or elevated temperatures, for example with the polyester at a temperature of from 20°C to 150°C but, in general, temperatures of from 90°C to 130°C are preferred.

The purification procedure in its simplest form comprises stirring the mixture of synthetic magnesium silicate and active carbon with the polyether at the desired temperature but any conventional method of treating a liquid with a small proportion of a solid may be employed. Thus, the polyether may be passed through a column packed with the required mixture. It is preferred to carry out the treatment under reduced pressure to minimise oxidation of the polyether and to ensure that the purified material has a low moisture content.

When the treatment is complete, the synthetic magnesium silicate and active carbon may be removed from the polyether by any convenient means, for example filtration at an elevated temperature.

Compared with polyethers requiring treatment in accordance with the present invention, treated polyethers show reduced cloudiness at ambient temperatures and higher cloud points. Treatment with synthetic magnesium silicate alone or with active carbon alone does not have the same effect.

The process of the invention is particularly useful for the purification of polyether polyols which are to be used in the manufacture of polyurethanes by reaction with organic polyisocyanates. The polyurethanes may be in the form of elastomers, foams, rigid plastics, coatings etc.

The invention is illustrated but not limited by the following Example in which all parts and percentages are by weight unless otherwise stated.

Example.

Samples of an ethylene oxide tipped oxypropylated glycerol, (molecular weight 5,300 oxyethylene content 14%) which had a degree of cloudiness believed to be caused by crystallisation of polyethylene glycol were treated as described in the Table below with the results also given in the Table.

Cloud points were determined by mixing 10 mls of the polyether under test with 10 mls of a 50/50 mixture of isopropanol/water in a boiling tube. This was placed in a beaker containing water at ambient temperature and the whole heated slowly. The mixture was stirred and the cloud point temperature was taken as that temperature at which the filament of a low, wattage 'pearl' bulb, approximately 1 ft. from the boiling tube, was no longer visible.

Method of Treatment	Appearance of treated polyol on standing for three days	Cloud point °C
Untreated	Cloudy	20
Stirred with 3% by wt. of Ambosol at 120°C for 2 hrs. at 20 mm Hg pressure. Filtered.	Cloudy	20
Stirred with 1.5% by wt. Actibon S at 120°C for 2 hrs. at 20 mm Hg pressure. Filtered.	Cloudy	43.9
Stirred with 3% by wt. of Ambosol and 0.5% Actibon S at 120°C for 2 hrs. at 20 mm Hg pressure. Filtered.	Clear	50.0

The effect of using mixed Ambosol/Actibon S is shown by the removal of cloudiness and improvement in cloud point.

The treatment may be carried out by several applications at a low level of mixed Ambosol/Carbon e.g. 5 × 1.25% Ambosol/0.25% Actibon S or one application at a high level e.g. 7.5% Ambosol/1.5% Actibon S. The number of applications and the level of treatment depends on the degree of cloudiness in the polyether polyol.

Ambosol is a grade of synthetic magnesium silicate available from Hoechst Chemicals.

Actibon S is a grade of active carbon available from the Norit Clydesdale Co. Ltd.

WHAT WE CLAIM IS:—

1. A process for the purification of polyethers which are the liquid reaction products obtained by the sequential addition of ethylene oxide and at least one other alkylene oxide to an active hydrogen-containing compound, said process comprising treating the polyether with a mixture containing 1 part by weight of active carbon and from 2.5 to 7.5 parts by weight of synthetic magnesium silicate.

2. A process as claimed in claim 1 wherein the polyether contains at least two hydroxyl groups per molecule and is made by the addition of ethylene oxide and propylene oxide to a compound containing at least two active hydrogen atoms in the molecule.

3. A process as claimed in claim 1 or claim 2 wherein the polyether has a molecular weight of from 1000 to 10,000 and an oxyethylene content of from 5 to 50% by weight based on the total oxyalkylene content.

4. A process as claimed in any one of the preceding claims wherein the polyether is treated with from 0.5 to 15% by weight of the mixture based on the weight of polyether.

5. A process as claimed in any one of the preceding claims wherein the mixture contains from 4.5 to 6.5 parts by weight of synthetic magnesium silicate for each part by weight of active carbon.

6. A process as claimed in claim 1 substantially as hereinbefore described with reference to the foregoing Example.

7. A polyether whenever purified by a process claimed in any one of the preceding claims.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1977.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.